

It is also interesting to point out that extrapolation to 100% P_{gg} and 100% $P_{g'g'}$ yields ${}^4J_{P-4'}$ values of 2.8 and 3.5 Hz, respectively, which in view of the uncertainty of Σ and Σ' values for the pure $gg-g'g'$ state may be considered to be in good agreement with the Hall²⁻⁴ estimates for W coupling in phosphate esters and with Duval, *et al.*,^{15,16} on acyclic esters. It is also noteworthy that a negative ${}^4J_{P-4'}$ (-0.8 Hz) is predicted for a β -5'-nucleotide with $P_{gg} = 0\%$. As yet no negative ${}^4J_{PH}$ coupling has been reported in phosphate esters,¹⁷ though on the basis of the conformational dependence of the sign of ${}^4J_{HCCCH}$ in propane^{18,19} a negative ${}^4J_{P-4'}$ for a g/t β -5'-nucleotide may not be unexpected.²⁰

Figures 1a and b can be of some practical value since they may provide crude estimates of Σ and Σ' (as well as P_{gg} and $P_{g'g'}$) from ${}^4J_{P-4'}$ and may be useful in those situations where the 5'5'' regions defy analysis. We stress caution in the application since additional splitting (broadening) in the 4' region can arise from virtual coupling.²¹ However, we may safely predict that if ${}^4J_{P-4'}$ is >1.0 Hz, the predominant conformer is $ggg'g'$, whereas if ${}^4J_{P-4'}$ is small (<0.3 Hz) it is predominantly $g/t-g'g'$ with a smaller (but not an insignificant) contribution from $g/t-t'/g'$. We realize that a small ${}^4J_{P-4'}$ is not inconsistent with $gg-t'/g'$. However, our $\Sigma\Sigma'$ correlations¹² as well as our ${}^4J_{P-4'}$ correlations demonstrate that this situation is not accessible to β -5'-nucleotides and is in agreement with X-ray studies on β -5'-nucleotides, dinucleoside monophosphates, RNA, and DNA,²¹⁻²⁶ as well as with steric consideration.

(17) A -0.55 -Hz ${}^4J_{HCCOP}$ has been reported for triethyl phosphate.¹²

(18) M. Barfield, *J. Amer. Chem. Soc.*, **93**, 1066 (1971).

(19) T. Schaefer and R. Wasylishen, private communications.

(20) It is meaningless to extrapolate the Σ' , ${}^4J_{P-4'}$ plot to $P_{g'g'} = 0\%$ since this work in conjunction with earlier studies⁹ demonstrates that for β -5'-nucleotides, the minimum $P_{g'g'}$ is about 65% and occurs for $P_{gg} = 0\%$; this puts a purely $g/t-t'/t'$ situation into a forbidden domain.

(21) For instance, when the ratio of the chemical-shift difference between H-2' and H-3' and $J_{2',3'}$ is small, ${}^{31}P$ decoupling experiments confirm the presence of ${}^4J_{P-4'}$.

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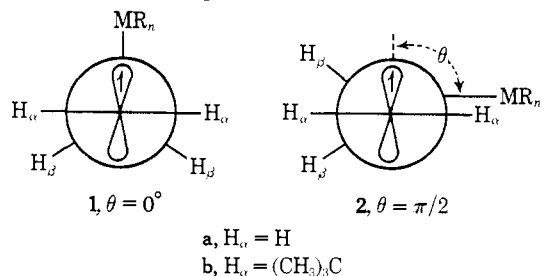
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Hyperconjugation in β -Substituted Ethyl Radicals. Does It Determine Conformation?¹

Sir:

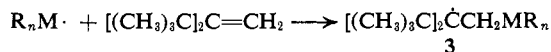
The conformations of β -substituted ethyl radicals, $R_nMCH_2CH_2\cdot$, as determined from the hyperfine splittings due to the β -hydrogens in their epr spectra, are of two principal types. If the atom M is from rows 2, 3, or 4 of the periodic table the most stable confor-

mation (*i.e.*, that favored at low temperatures) is **1a**, while if M is from row 1 the most stable conformation is **2a**.²⁻¹⁴ For example,² with $R_nM = Et_3Si$ conformation **1a** obtains and with $R_nM = H_3C$ conformation **2a** obtains at low temperatures.¹⁵



Kochi and Krusic² proposed that **1a** is favored over **2a** for second-row elements because of 1,3 bonding between the unfilled 3d orbitals of M and the 2p orbital of the carbon radical center (p-d homoconjugation). The subsequent discovery^{3,4,7} of unusually large hyperfine coupling to M led to proposals of a hyperconjugative delocalization mechanism between the C_α 2p orbital and the C_β -M σ bond; orbital overlap being maximized in conformation **1a**. Lyons and Symons^{3,4} favor hyperconjugation *alone*¹⁶ and point out that **1a** is favored when $R_nM\cdot$ is a pyramidal radical since hyperconjugative contributions of the type $\dot{C}-C-MR_n \leftrightarrow C=C\cdot MR_n$ require smaller changes in geometry of the R_nM group than when $R_nM\cdot$ is a planar radical.

We have discovered that a series of relatively long-lived ($\tau_{1/2}$ ca. 5 sec at 25°) carbon centered radicals can be formed by radical addition to 1,1-di-*tert*-butylethylene in solution



The longevity of these radicals (which is conferred by the di-*tert*-butyl moiety¹⁷) allowed accumulation of sufficient concentrations that hyperfine splittings owing to ${}^{13}C$ in natural abundance could often be measured. The epr parameters of a few representative radicals of type **3** (see Table I) imply that hyperconjugation *alone* is not sufficient to account for the conformational preferences of row 1 and row 2 R_nM adducts to ethylene.

The low values of $a^{H\beta}$ imply that all **3** prefer conformation **1b** even at room temperature.¹⁸ Having

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(4) A. R. Lyons and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, **68**, 622 (1972).

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(7) T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 648 (1972).

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(10) D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6486 (1972).

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(12) T. Kawamura, D. J. Edge, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 1752 (1972).

(13) M. C. R. Symons, *Chem. Phys. Lett.*, **19**, 61 (1973).

(14) J. Cooper, A. Hudson, and R. A. Jackson, *Tetrahedron Lett.*, 831 (1973).

(15) Conformations intermediate between **1a** and **2a** are also possible.^{9,10}

(16) The occurrence of C_α -M, p-p homoconjugation when M has lone pairs of electrons appears to be generally accepted.¹¹⁻¹⁴

(17) See G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 3422 (1973).

(18) $R_nMCH_2\dot{C}(CH_3)_2$ in conformation **1** have $a^{H\beta} \approx 11.4$ G.²

(1) Issued as NRCC No. 13457.

Table I. Epr Parameters for $[(\text{CH}_3)_3\text{C}]_2\dot{\text{C}}\text{CH}_2\text{MR}_n$ and Related Radicals at 20° and Calculated Spin Densities at M (a Values in G)

Radical ^a	g	$a^{\text{H}\beta}$	$a^{13\text{C}\gamma_{(\text{CH}_3)_3\text{C}}^b}$	$a^{\text{H}\gamma_{(\text{CH}_3)_3\text{C}}}$	$a^{13\text{C}\alpha}$	a^{M}	a^{R}	ρ_σ
3a $\text{B}_2\dot{\text{C}}\text{CH}_2\text{CF}_3$	2.0026	12.16	11.53	0.45	45.45	30.08	0.90	0.108
3b $\text{B}_2\dot{\text{C}}\text{CH}_2\text{CCl}_3$	2.0034	10.68	10.44	0.42	45.57	34.0	2.1	0.122
3c $\text{B}_2\dot{\text{C}}\text{CH}_2\text{SiMe}_3$	2.0025	15.76	10.23	0.36	46.35	35.02		0.116
3d $\text{B}_2\dot{\text{C}}\text{CH}_2\text{SiBu}_3^n$	2.0024	15.78	10.10	<i>c</i>	47.38	30.87		0.102
3e $\text{B}_2\dot{\text{C}}\text{CH}_2\text{SiCl}_3$	2.0030	14.58	<i>c</i>	0.43	<i>c</i>	77.24	2.2	0.255
$\text{B}_2\dot{\text{C}}\text{H}^{d,e}$	2.0027		12.25 ^f	0.68	42.98 ^f			0.084 ^g
$\text{B}_3\dot{\text{C}}^{d,e}$	2.0025		10.99 ^f	0.51 ^f	51.10 ^f			0.079 ^g

^a $\text{B} = (\text{CH}_3)_3\text{C}$ group. ^b $a^{13\text{C}\beta}$ must be $\leq a^{13\text{C}\gamma_{(\text{CH}_3)_3\text{C}}}$ for all three β carbons since it could not be detected in most of the above radicals. ^c Not resolved. ^d Data from ref 17 unless noted. ^e $a^{\text{H}\alpha} = 21.89$. ^f Measured for this work. ^g Value for $\text{B}_2\dot{\text{C}}\text{CH}_2\text{CH}_3$. Calculation of ρ_σ is based on the assumption that $a^{13\text{C}\gamma_{(\text{CH}_3)_3\text{C}}$ for $\text{B}_2\dot{\text{C}}\text{H}$ and $\text{B}_3\dot{\text{C}}$ would be half as large as a^{M} for $\text{B}_2\dot{\text{C}}\text{CH}_2\text{CH}_3$ in conformation 1 since the *tert*-butyl groups in these two radicals rotate freely.

established the conformation of **3** we wish to concentrate on the proportion of unpaired electron density, ρ_σ , which is delocalized into the $\text{C}_\beta\text{-M}$ bond by hyperconjugation. This may be calculated from a^{M} using the equation^{4,7}

$$\rho_\sigma = 4a^{\text{M}}/a_0^{\text{M}}$$

where a_0^{M} is the coupling constant for M with unit unpaired electron density in its valence shell s atomic orbital.¹⁹ Taking $a_0^{13\text{C}} = 1110$ G and $a_0^{29\text{Si}} = 1207$ G yields the ρ_σ values²⁰ listed in Table I.

The ρ_σ values for particular M tend to increase with increasing electronegativity of R (compare estimated value for $\text{R}_n\text{M} = \text{CH}_3$ ²¹ with **3a** and **3b**, and also **3c** and **3d** with **3e**). However, the significant factor is that when the groups CF_3 and CCl_3 are constrained by the di-*tert*-butyl moiety so that conformation **1** applies, their ρ_σ values and hence the extent of their hyperconjugative interactions are essentially the same as for the Me_3Si and Bu^n_3Si groups. Since, in the simple ethylene adducts only the silicon centered groups adopt conformation **1**²² while the carbon centered groups adopt conformation **2**,²³ it must be concluded that hyperconjugation *alone* is not sufficient to hold β -tri-alkylsilyl ethyl radicals in conformation **1** and that some additional factor, *e.g.*, p-d homoconjugation,¹⁰ provides the force required to stabilize this conformation.

We are not unaware that additional conclusions concerning **3** can be drawn from the epr parameters in Table I. However, for the present we would merely point out that the $a^{13\text{C}\alpha}$ values support Symons' conclusion²⁷ that an $a^{13\text{C}\alpha} \approx 46$ G for *tert*-butyl should not be cited as evidence for the nonplanarity of *tert*-butyl.²⁸ That is, it seems highly unlikely that the rad-

(19) Although approximate sp^3 hybridization of M is hereby assumed, fairly large changes in the s:p ratio would not substantially affect our conclusions.

(20) Calculated (ignoring difference in g factor) from data listed by J. E. Werz and J. R. Bolton in "Electron Spin Resonance," McGraw-Hill, New York, N. Y., 1972.

(21) See footnote g of Table I. We were unsuccessful in attempts to add CH_3 to di-*tert*-butylethylene.

(22) For $\text{Et}_3\text{SiCH}_2\text{CH}_2$ at -112° $a^{\text{H}\beta} = 17.67$ G, $a^{29\text{Si}} = 37.4$ G,^{2,7} and for $\text{Cl}_3\text{SiCH}_2\text{CH}_2$ $a^{\text{H}\beta} = 17.22$ G.¹⁰

(23) For $\text{Cl}_3\text{CCH}_2\text{CH}_2$ between -20 and -160° $a^{\text{H}\beta} = 22.3$ G,¹⁰ for $\text{CF}_3\text{CH}_2\text{CH}_2$ $a^{\text{H}\beta} = 26.30$ G^{24,25} at -120° .

(24) D. Griller, unpublished results.

(25) Values of $a^{\text{F}\beta}$ for $\text{CF}_3\dot{\text{C}}\text{F}_2$ and $\text{CF}_3\text{CF}_2\dot{\text{C}}\text{F}_2$ (11.2 and 15 G, respectively²⁶) imply that the latter radical also prefers conformation **2**.

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(27) M. C. R. Symons, *Mol. Phys.*, **24**, 461 (1972); *Tetrahedron Lett.*, 207 (1973).

(28) D. E. Wood, L. F. Williams, R. F. Sprecker, and W. A. Lathan, *J. Amer. Chem. Soc.*, **94**, 6241 (1972).

icals we report, which contain extremely bulky ligands, could be anything but planar. Values of $a^{13\text{C}\alpha}$ increase from 38.34 G for CH_3 ,²⁹ to 39.07 G for $\text{CH}_3\text{-}\dot{\text{C}}\text{H}_2$,²⁹ to 41.3 G for cyclohexyl,²⁹ to 43 G for $[(\text{CH}_3)_3\text{C}]_2\dot{\text{C}}\text{H}$, and to *ca.* 46 G for tertiary carbon radicals.

Acknowledgment. We are extremely grateful to Professor T. T. Tidwell for a generous sample of 1,1-di-*tert*-butylethylene.

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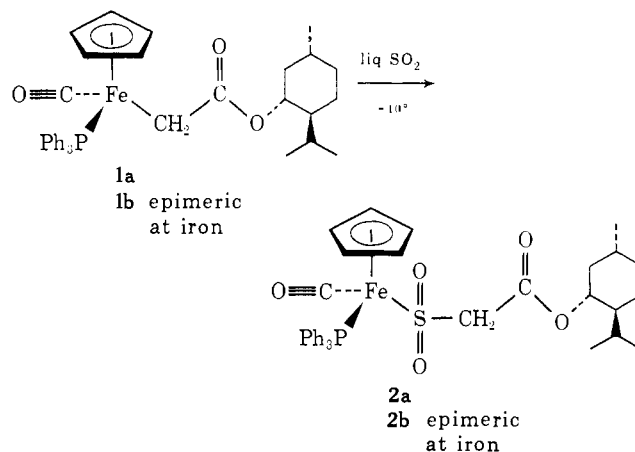
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Stereochemistry at Iron of the Insertion of SO_2 into the Iron-Carbon σ Bond

Sir:

Considerable interest centers around the mechanisms of reaction of the metal-carbon σ bond because of their relevance to catalytic systems.¹ We report herein the synthesis and resolution of the iron-carbon σ -bonded compound **1** and describe the first example of the use of such a molecule to establish the stereochemistry at the metal resulting from reaction of the iron-carbon bond. The insertion reaction of **1** with liquid sulfur dioxide has been found to proceed with a high degree of stereospecificity at iron.



(1) M. L. H. Green, "Organometallic Compounds," Vol. 2, Methuen, London, 1968, Chapters 7 and 9; C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967.